

# Growth of InSb and InI crystals on Earth and in Microgravity



Aleksandar Ostrogorsky,

**Alexei V. Churilov**, RMD  
Watertown, MA

**Martin P. Volz**  
NASA MSFC, Huntsville, AL

**V. Riabov**, IIT

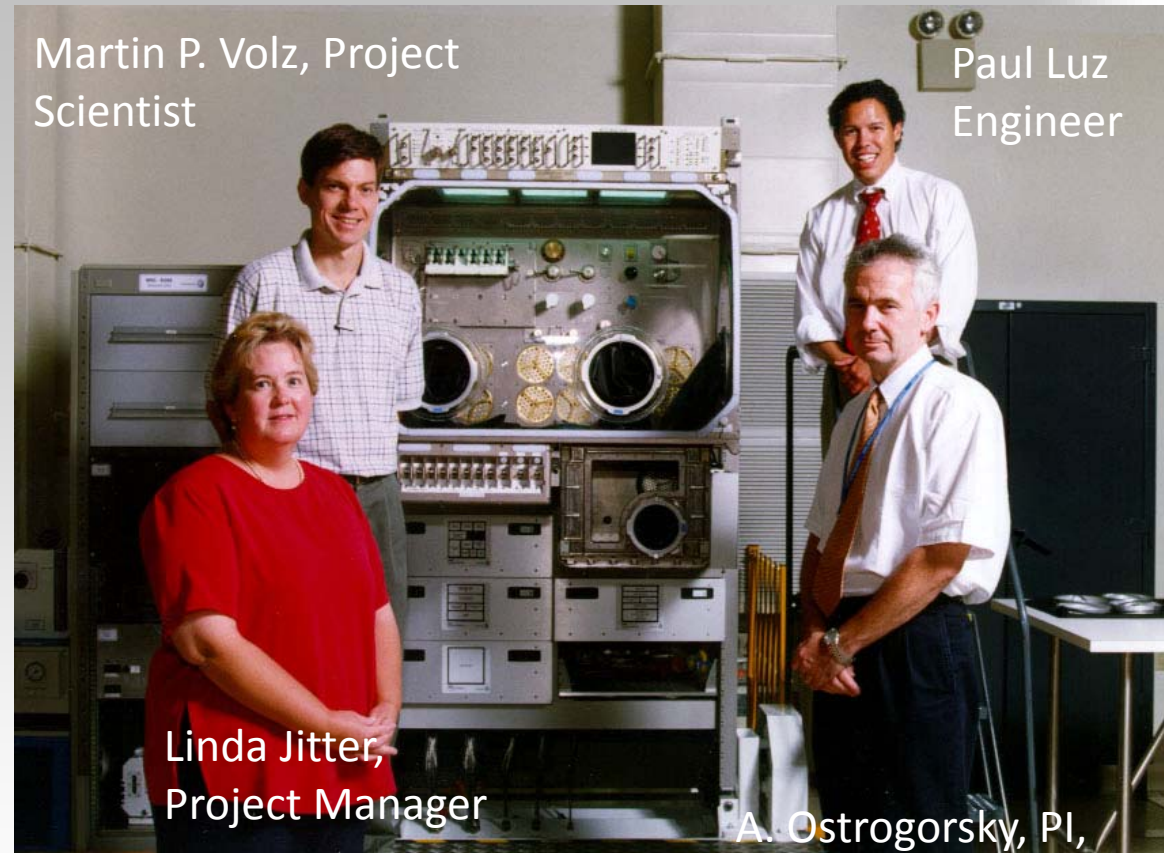
**Dr. Lodewijk van den Berg**,  
Constellation Technology Largo FL

- 
1. *Te and Zn doped InSb: NASA (1995-2004)*
  2. *InI DoE NNSA (2005-2015);  
CASIS/NASA (2015-2017)*



## *SUBSA: Solidification Using a Baffle in Sealed Ampoules*

- 1995-2004
- SCR 1998
- Design review 2000
- Endeavour, Expedition 5, 2002.
- Seven Te- and Zn-doped InSb crystals were grown.



# SUBSA Design review 6/8/2000

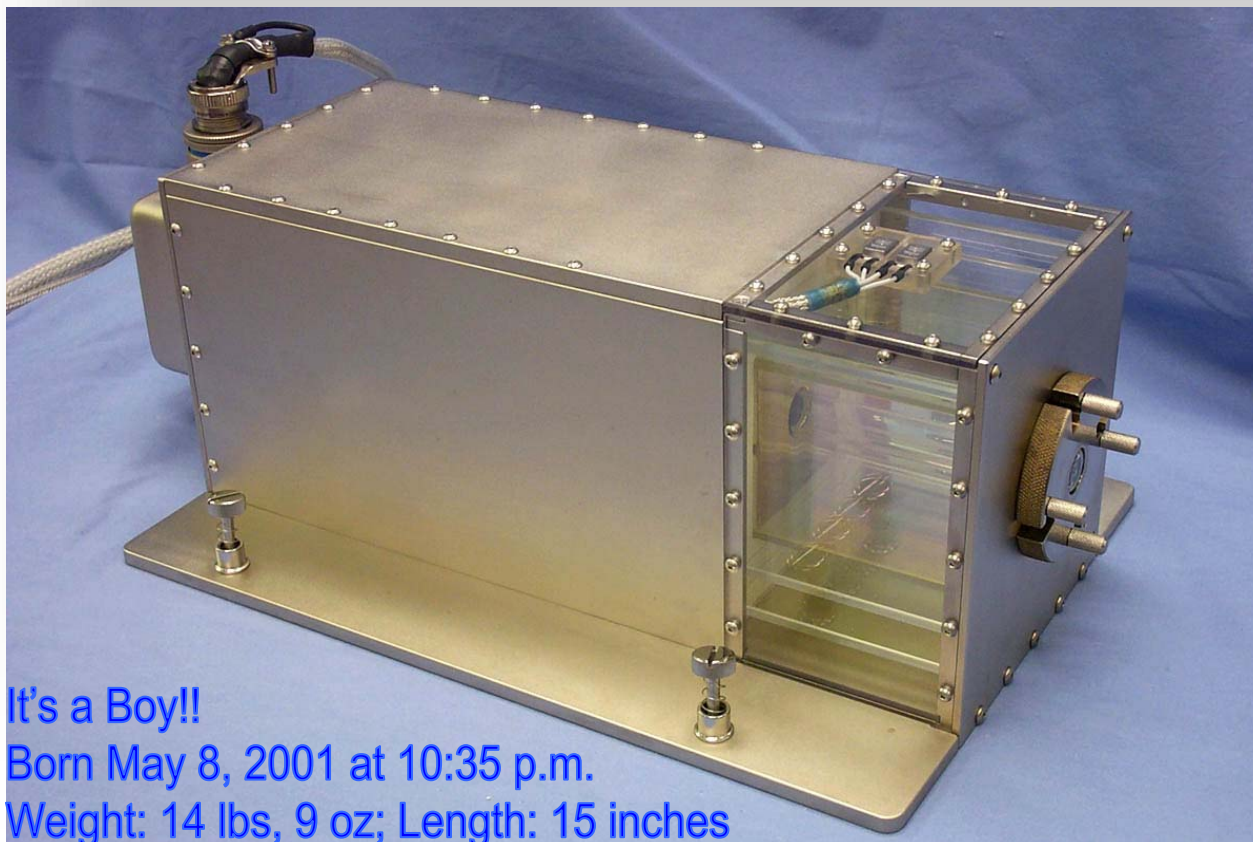


# SUBSA HARDWARE AT AT GLANCE

TecMasters Inc



**LabVIEW 6i processes data on MSG Laptop Computer**



**1 DaqPad**

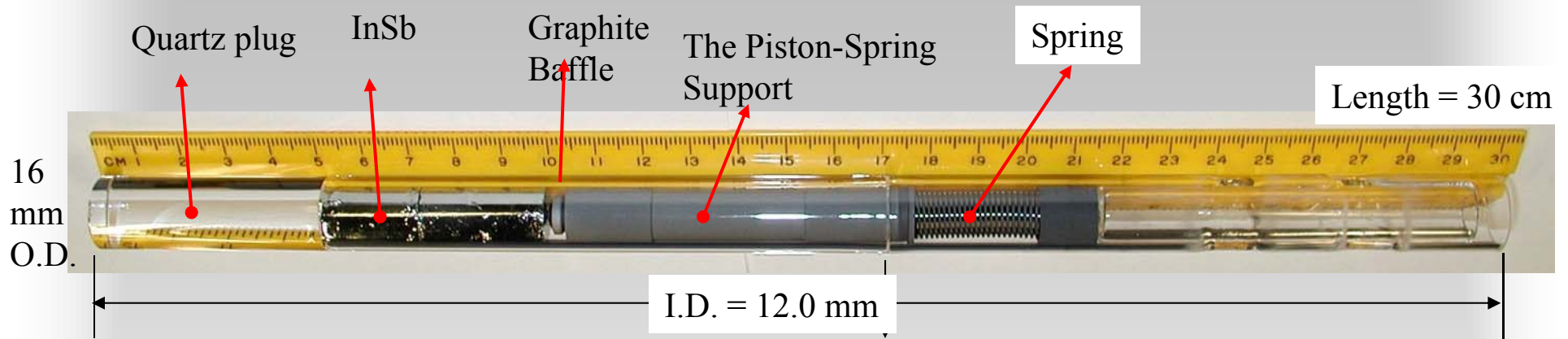


**1 Process Control**

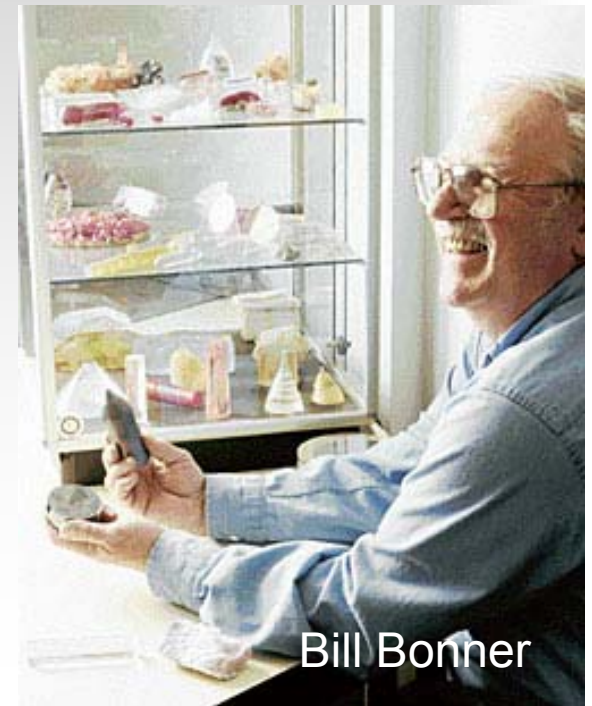


**Video Camera**

# SUBSA AMPOULE ASSEMBLY

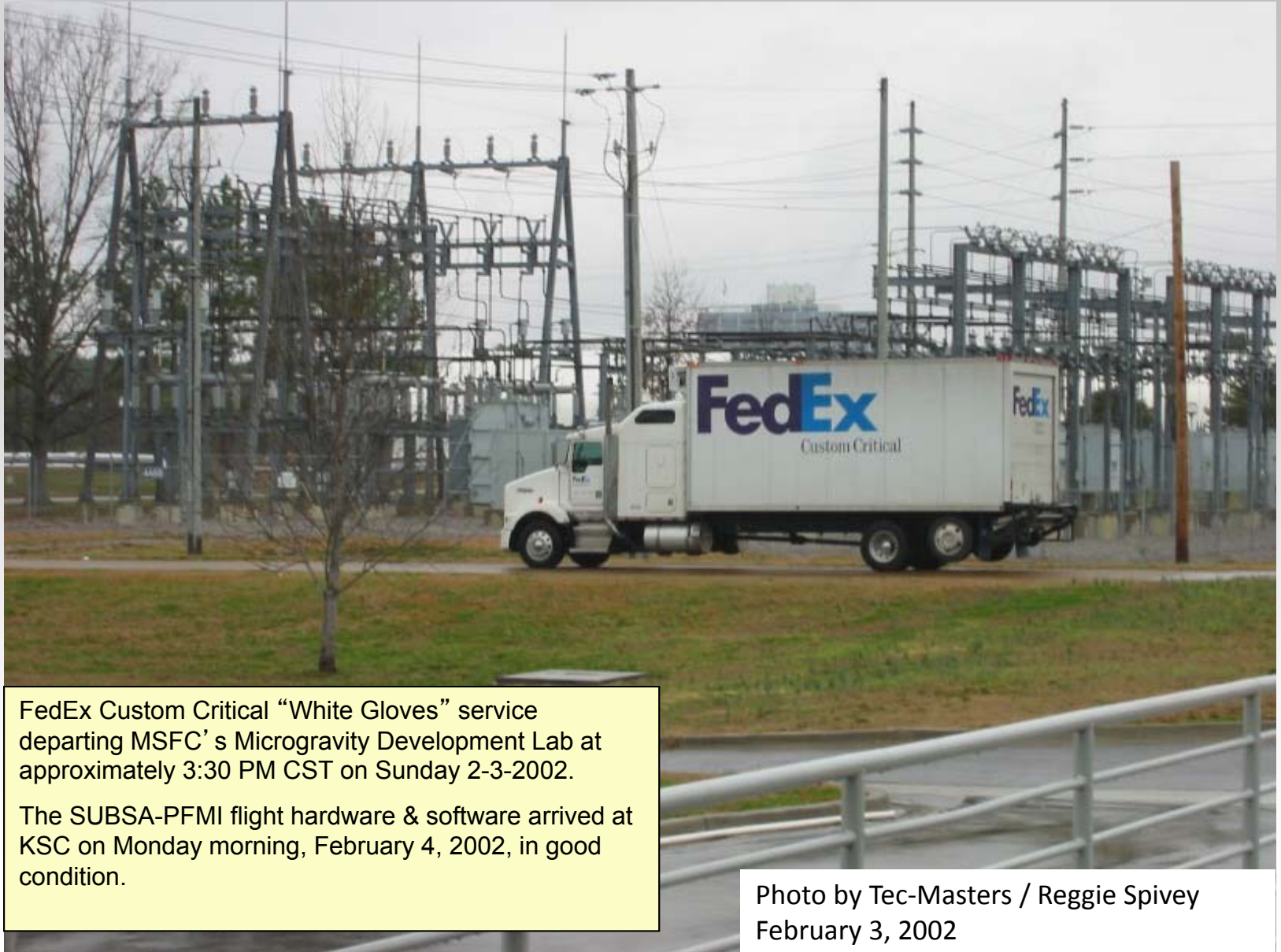


- InSb seed
- 50g InSb, doped with Te or Zn (**MP 512 C**)
- Sealed under vacuum.



Bill Bonner

# SUBSA Status on Sunday 2/3/2002



FedEx Custom Critical “White Gloves” service departing MSFC’s Microgravity Development Lab at approximately 3:30 PM CST on Sunday 2-3-2002.

The SUBSA-PFMI flight hardware & software arrived at KSC on Monday morning, February 4, 2002, in good condition.

Photo by Tec-Masters / Reggie Spivey  
February 3, 2002

# Crew of the Expedition Five



June 5, 2002. Shuttle [Endeavour](#), Flight [UF-2](#) -STS-111



Valery Korzun  
Expedition commander

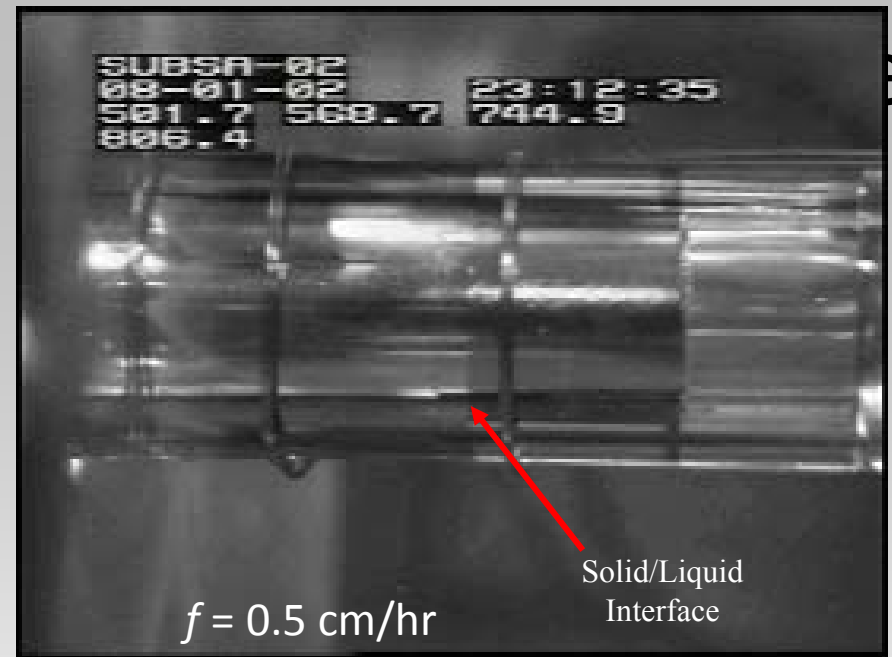
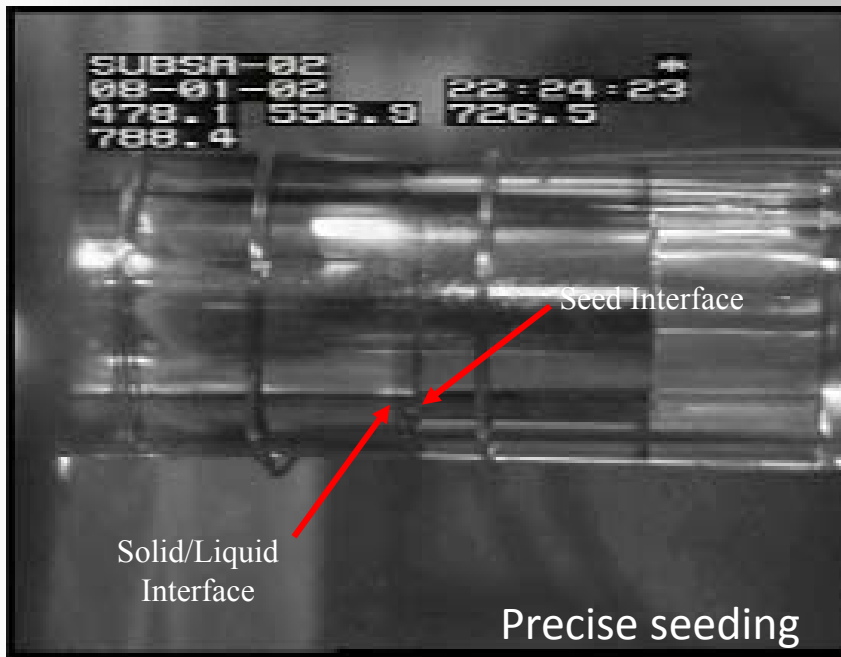


Dr. Peggy Whitson,  
flight engineer, USA,  
**payload specialist**



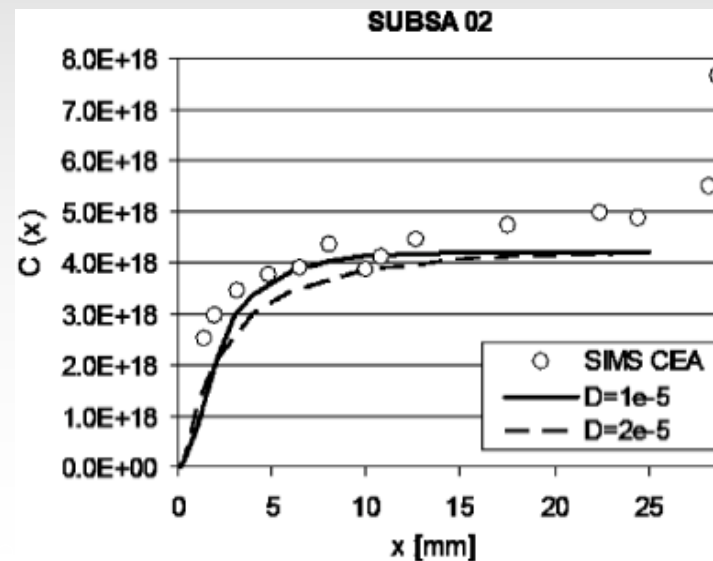
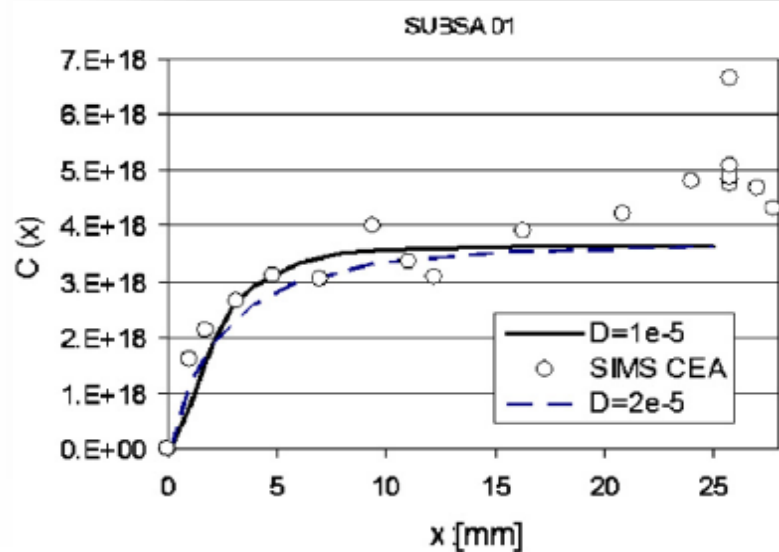
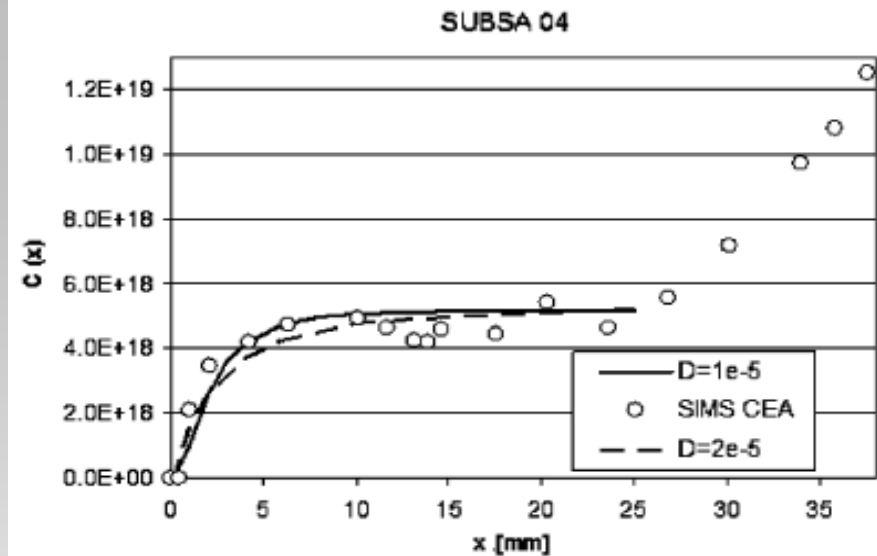
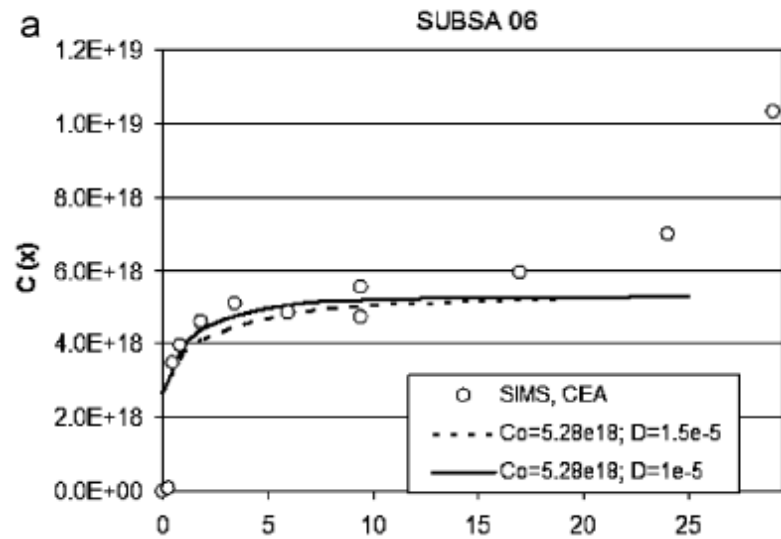
Sergei Treschev  
flight engineer

# CONTROL OF seeding and growth



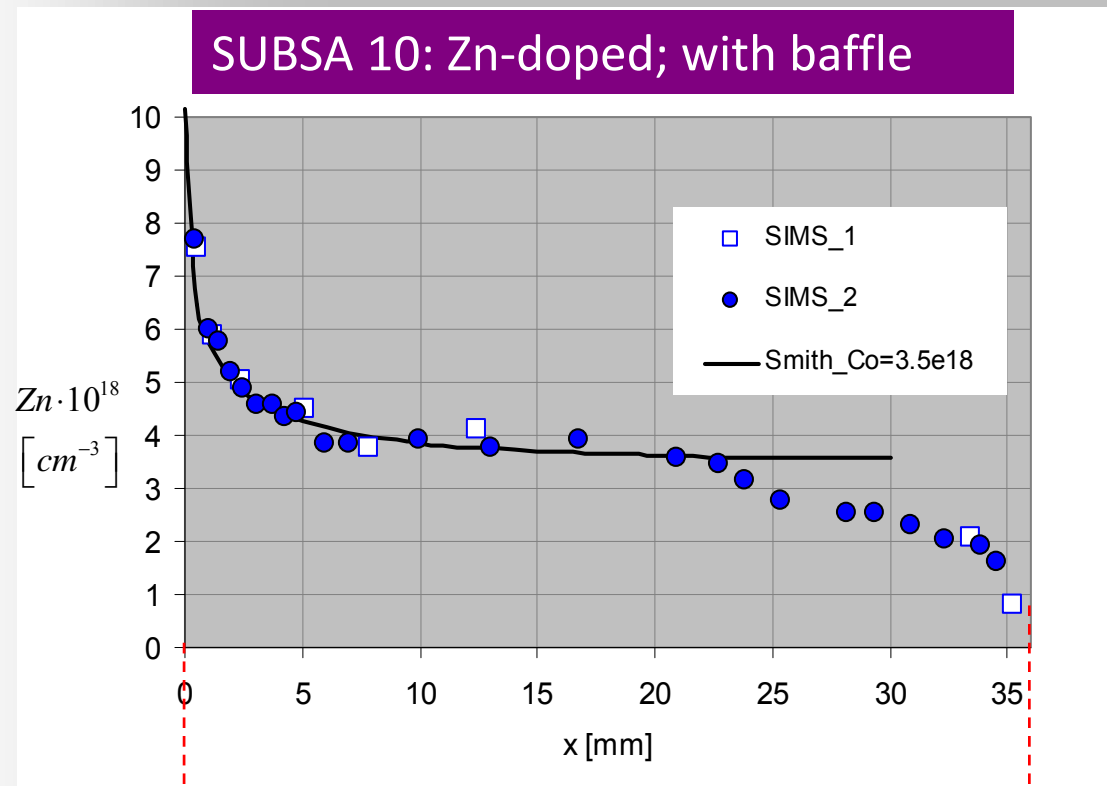
# Results SUBSA: Te-doped InSb

$$k_0 = 0.5 < 1$$



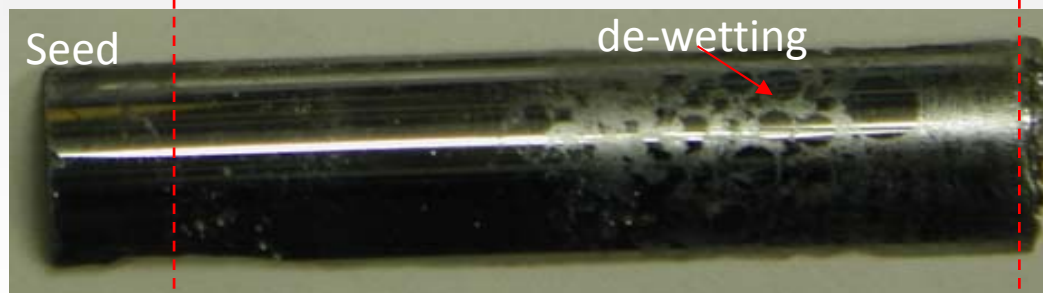
$$D = 1 \cdot 10^{-5} \left[ \frac{cm^2}{s} \right]$$

## Results SUBSA #10: Zn-doped InSb



Zn-doped  $\Rightarrow k_0 = 2.9 > 1$  !!

$k_0 > 1$  is proffered for growth in microgravity.



$$D = 1.2 \times 10^{-4} \text{ cm}^2/\text{s}$$

# Results – $k_{\text{eff}}$ model

*All previous equations are based on  $\delta$ :*

1. BPS (1953) **FC only**.
2. Wilson (1978)-Garandet (2008) **FC only**.
3. Ostrogorsky-Muller, (OM, 1992, lateral convection, **NC**)
4. Yen and Tiller (1992, lateral convection considered).

...

$$\frac{C_s}{C_L} = k_{\text{eff}}(\delta)$$

$$\delta = 1.6 D^{1/3} \nu^{1/6} \omega^{-1/2}$$

- *Laminar steady flow driven by a rotating disk*
- *$g$ -driven flow ignored.*

*Equation based on empirical correlations for Nusselt (or **Sherwood**) Numbers (Ostrogorsky, 2012)*

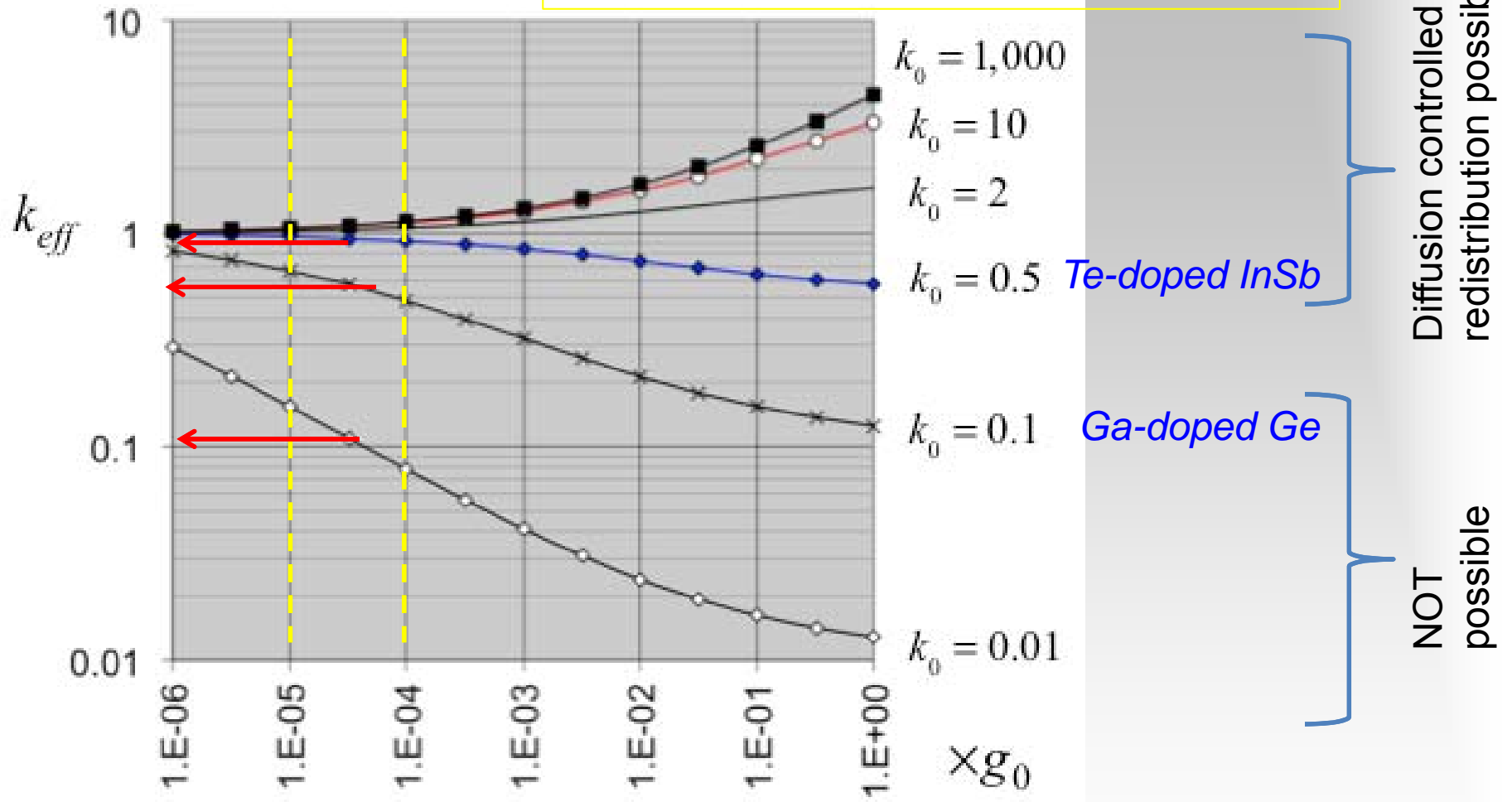
$$\frac{C_s}{C_L} = k_{\text{eff}}(k_0, \text{Nu}, Pe)$$

$$\text{Nu} \equiv \frac{h \cdot L}{D} = F(Gr, Pr, Sc)$$

$$\text{Gr} = \frac{g \beta \Delta T L^3}{\nu^2} = \frac{F_{\text{buoyancy}}}{F_{\text{viscous}}}$$

# $k_{eff}$ as a function of $k_0$ and $g$ - level

Ostrogorsky and Glicksman, Handbook of Crystal Growth (2014)



- Diffusion-controlled melt growth on orbital platforms is practical only with systems  $0.5 \leq k_0 \leq \infty$
- Not recognized in the 1970s and 1980s; attempts were made to grow *Sb-doped Ge* ( $k_0 = 0.003$ ) and *Sn-doped InSb* ( $k_0 = 0.057$ )



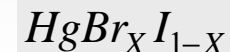
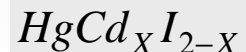
## HgI<sub>2</sub> (soft and grown from vapor phase)

- At in the vicinity of 130 ° C, **tetragonal red α-HgI<sub>2</sub>** crystals undergo a destructive phase transition to an **orthorhombic yellow β-HgI<sub>2</sub>** phase

Material	CdTe	ZnTe	Cd <sub>0.9</sub> Zn <sub>0.1</sub> Te	HgI <sub>2</sub>	CdI <sub>2</sub>	HgBr <sub>2</sub>	InI
Av. Atomic Z <sub>eff</sub>	50.16	46.21	49.1	59.9	51.3	50	51
ρ (g/cm <sup>3</sup> )	5.85	6.34	5.78	6.4	5.640	6.05	5.31
Eg. (eV)	1.56	2.25	1.549	2.41	3.5	3.6	2.0
ρ [ <u>Ω</u> cm]	~10 <sup>9</sup>		3x10 <sup>9</sup>	10 <sup>13</sup>			~10 <sup>11</sup>



GOALS: Investigate the potential of high-Z number binary and ternary iodides that have not received sufficient attention.



# REQUIREMENTS FOR RT DETECTORS

Room Temperature (RT) operation requirements

energy gap:  $1.5 \text{ eV} < E_g < 2.5 \text{ eV}$

$Z > 50$

		II	III	IV	V	VI		
								Helium 4.002 60
		Group 13		Group 14		Group 15		Group 16
		5 <b>B</b> Boron 10.811	6 <b>C</b> Carbon 12.0107	7 <b>N</b> Nitrogen 14.0067	8 <b>O</b> Oxygen 15.9994	9 <b>F</b> Fluorine 18.998 4032	10 <b>Ne</b> Neon 20.1797	
		13 <b>Al</b> Aluminum 26.981 5386	14 <b>Si</b> Silicon 28.0855	15 <b>P</b> Phosphorus 30.973 762	16 <b>S</b> Sulfur 32.065	17 <b>Cl</b> Chlorine 35.453	18 <b>Ar</b> Argon 39.948	
Group 11	Group 12	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.409	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.64	33 <b>As</b> Arsenic 74.921 60	34 <b>Se</b> Selenium 78.96	35 <b>Br</b> Bromine 79.904
		47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.411	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.904 47
		79 <b>Au</b> Gold 196.966 569	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.3833	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.980 40	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)
		111 <b>Rg</b> Roentgenium (272)	112 <b>Uub*</b> Ununbium (285)		114 <b>Uuq*</b> Ununquadium (289)		116 <b>Uuh*</b> Ununhexium (292)	

	Z	[eV]
Si	14	1.12
Ge	32	0.7
GaAs	33	1.43
InP	49	1.35
AlSb	51	1.6
CdTe	52	1.49
ZnTe	52	2.25
HgI <sub>2</sub>	80	2.13
HgBr <sub>2</sub>	80	3.6
PbI <sub>2</sub>	82	2.55
BiI <sub>3</sub>	83	1.75
TlBr	81	2.8
TlI	81	2.15
InI	53	2

III-V compounds

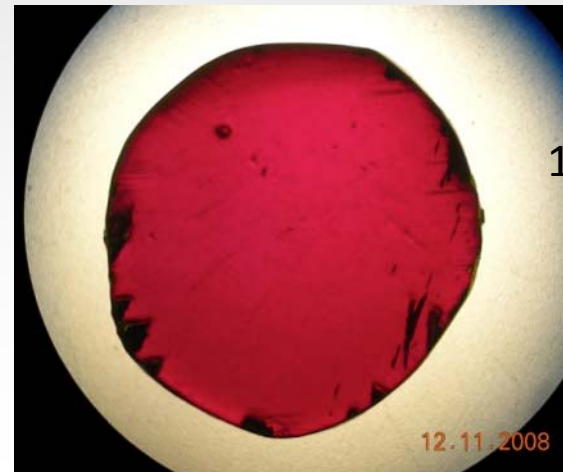
Cd<sub>0.8</sub>Zn<sub>0.2</sub>Te  
"CZT"

Best

Best

# WHY INDIUM IODIDE?

- Promising semiconductor RT detector material + not toxic; MP= 360 C (perfect for SUBSA furnace)
- Developed procedures for synthesis, ZR, melt growth, vapor growth
- RPI (2006-2009); IIT (2009-present), RMD (2015).
- DoE, NNSA

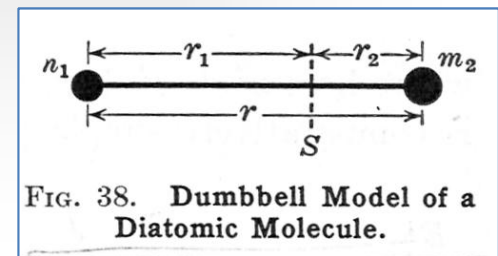


15 mm diameter

*Is CZ growth of InI possible ?*



	Disassociation Energy , eV
I <sub>2</sub>	1.542
Bil	0.3
Hgl	0.35
HgBr	0.71
CdTe	1.2
Pbl	2.0
PbBr	2.5
TII	2.76
TIBr	2.34
InI	3.43
InBr	3.9



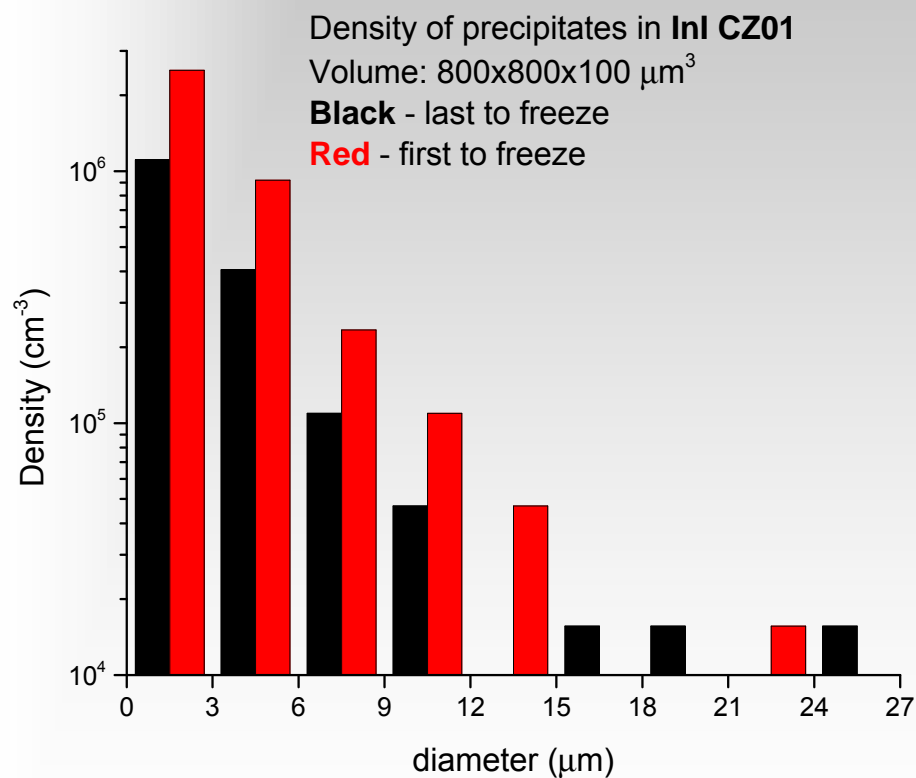
## CZOCHRALSKI GROWTH OF InI

- Detector materials have high vapor pressure; growth in sealed ampoules.
- **CZ growth of a detector crystal demonstrated for the first time**

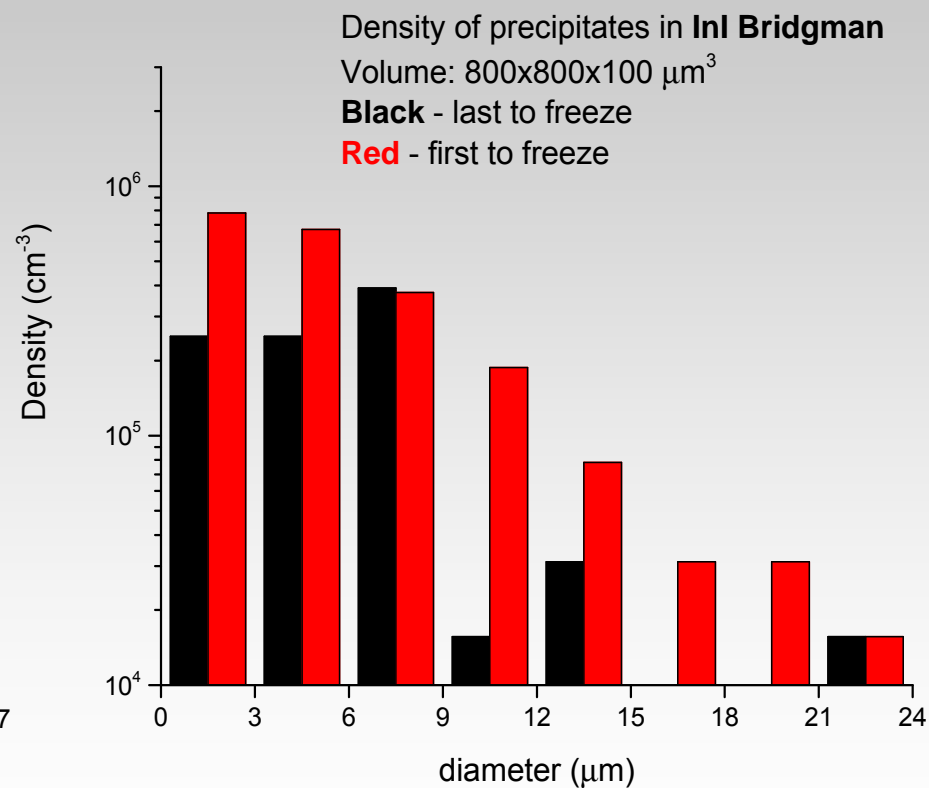


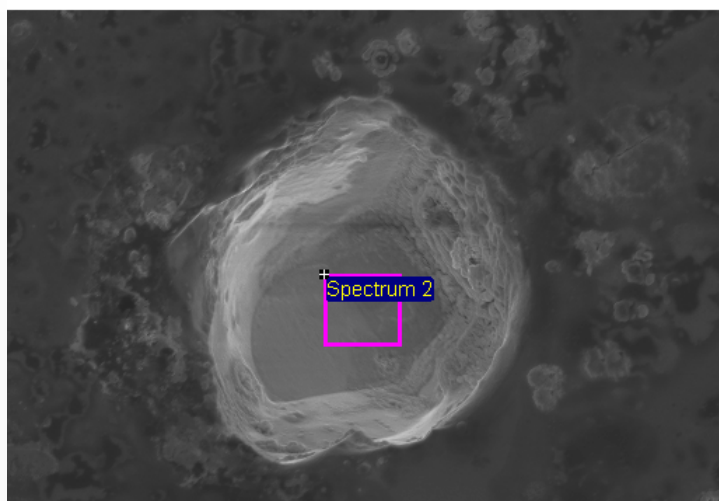
# DISTRIBUTION OF PRECIPITATES

## CZOCHRALSKI



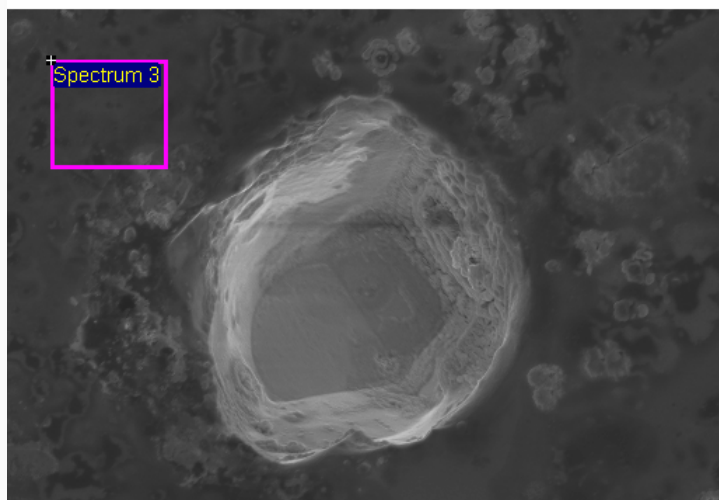
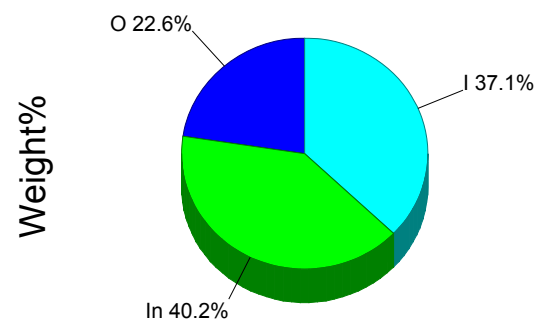
## BRIDGMAN





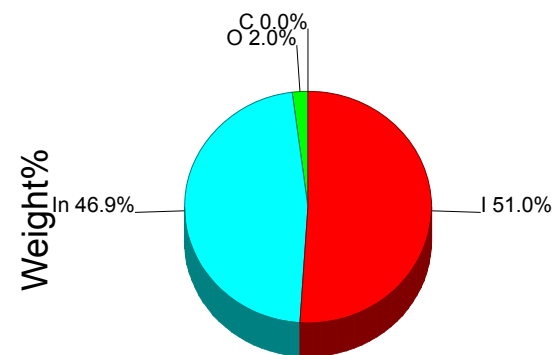
40µm

Electron Image 1



40µm

Electron Image 1



**High Purity Indium (In) Metal**  
Analysis by Glow Discharge Mass Spectrometry

<b>Tested by:</b>	Institute for National Measurement Standards, National Research Council
<b>Report Date:</b>	14-Jul-10
<b>Report NO:</b>	31810
<b>Lot Number:</b>	92

Element	Analytical Result in ppb(mass)
Mg	<0.1
Al	<0.2
Si	0.7
S	2.8
Fe	0.5
Ni	18.4
Cu	8.3
Zn	<1.7
Ga	<0.4
Ge	<0.6
Ag	<0.8
Cd	79.3
Sn	13.4
Tl	7.1
Pb	61.4
Bi	<0.9

<b>Total Detected Impurities:</b>	<b>191.9</b>
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Certificate of analysis iodine 5N  
metal basis (Alfa Aesar Inc.).

**Iodine lump, ultra dry, 99.999% (metals basis)**

**Stock Number: 44857**  
**Lot Number: J21W012**

**Analysis**

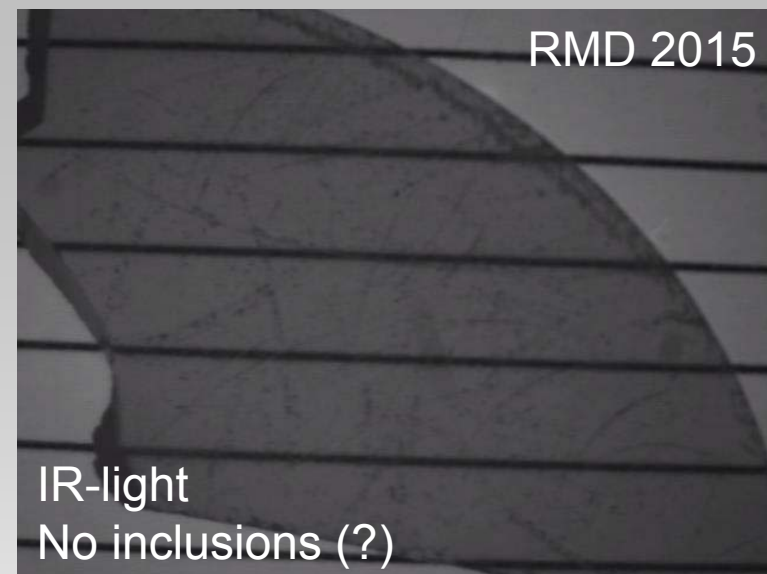
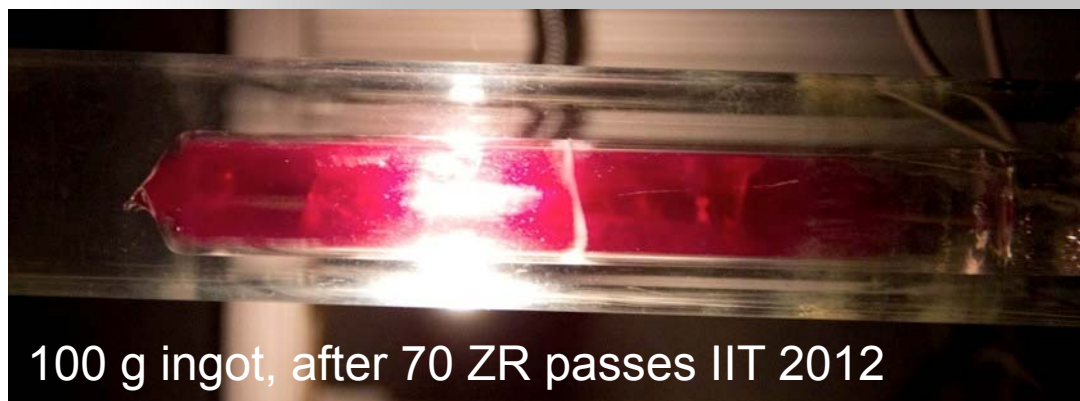
Purity > 99.999 % (metals basis)

Mg	<0.5	Mn	<0.2
Al	<0.2	Fe	<0.2
P	<0.1	Ni	<0.1
K	<0.1	Cu	<0.1
Ca	<0.1	Zn	<0.1
Ti	<0.1	As	<0.1
V	<0.1	Sn	<0.1
Cr	<0.1	Pb	<0.1

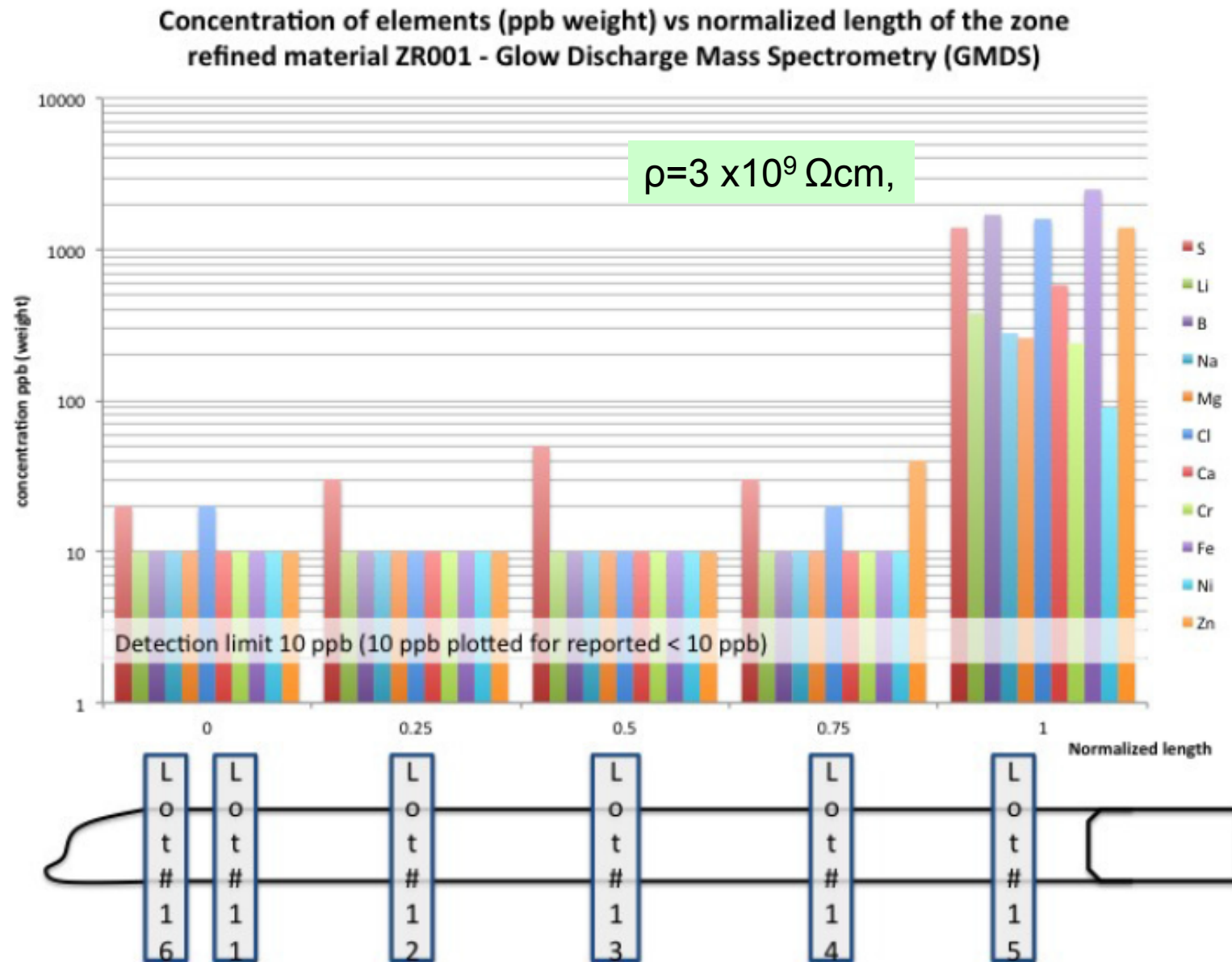
Values given in ppm unless otherwise noted  
All other impurities are lower than detection limits (<0.01 ppm)

Analysis method: Mass spectrometry

# PURIFICATION BY ZONE REFINING (ZR)

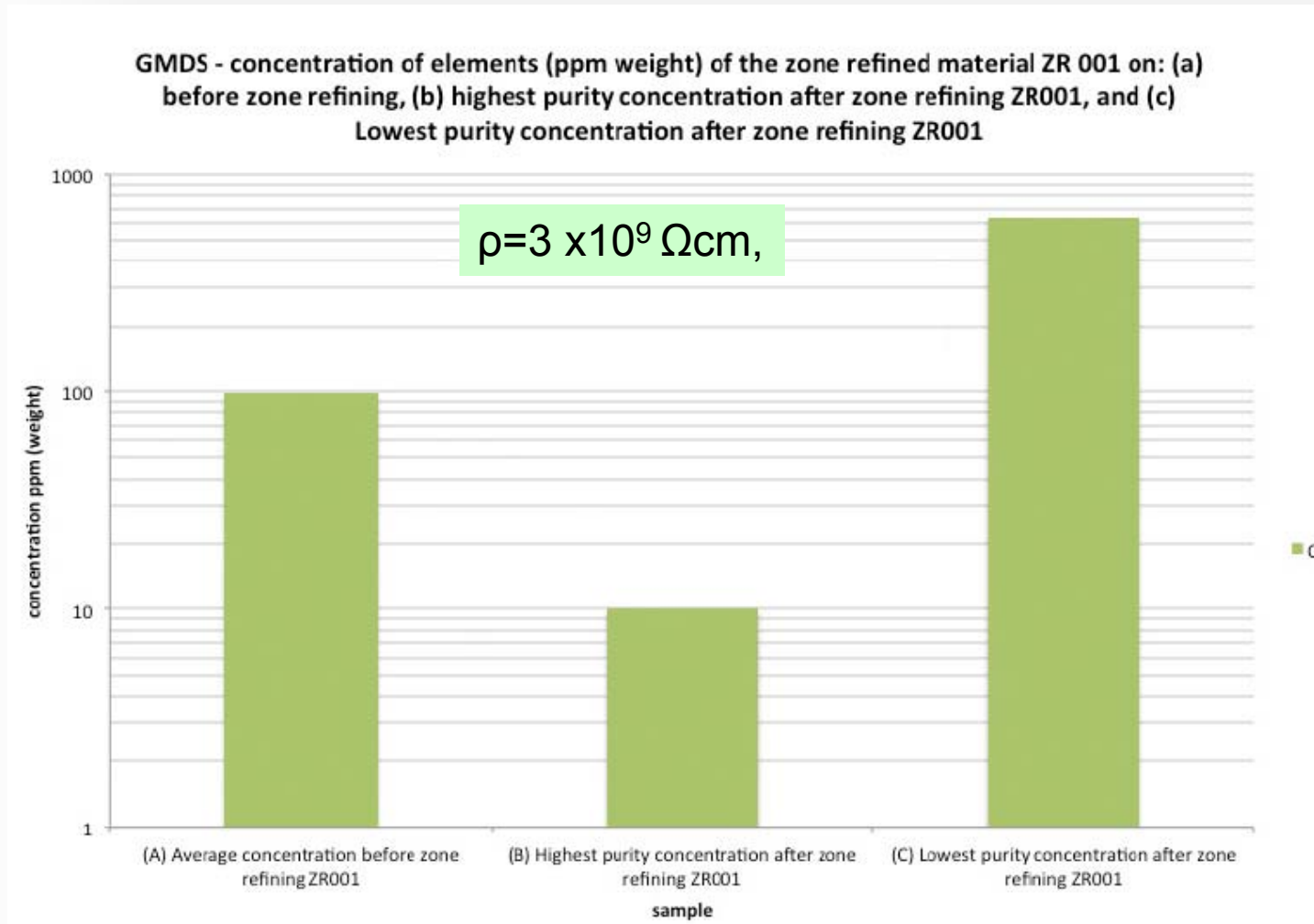


**350 g** ingot, was ZR and grown in an open boat, under dynamic gas flow  
5% H<sub>2</sub> + 95 % Argon, RMD 2015.



IIT 2012: Final concentration of S, Li, B, Na, Mg, Cl, Ca, Cr, Fe, Ni and Zn (ppb by weight) vs normalized length of the zone refined material ZR001 - Glow Discharge Mass Spectrometry (GMDS) by Evans Analytical Group.

# Instrumental Gas Analysis (IGA) by Evans Analytical Group.



Comparison of concentrations of oxygen (ppm by weight) of the zone refined (ZR) material ZR 001 on: (a) before zone refining, (b) highest purity concentration after ZR, and (c) Lowest purity concentration after ZR.

## 2012, IIT:

Concentration of oxygen and selected elements in ZR 001

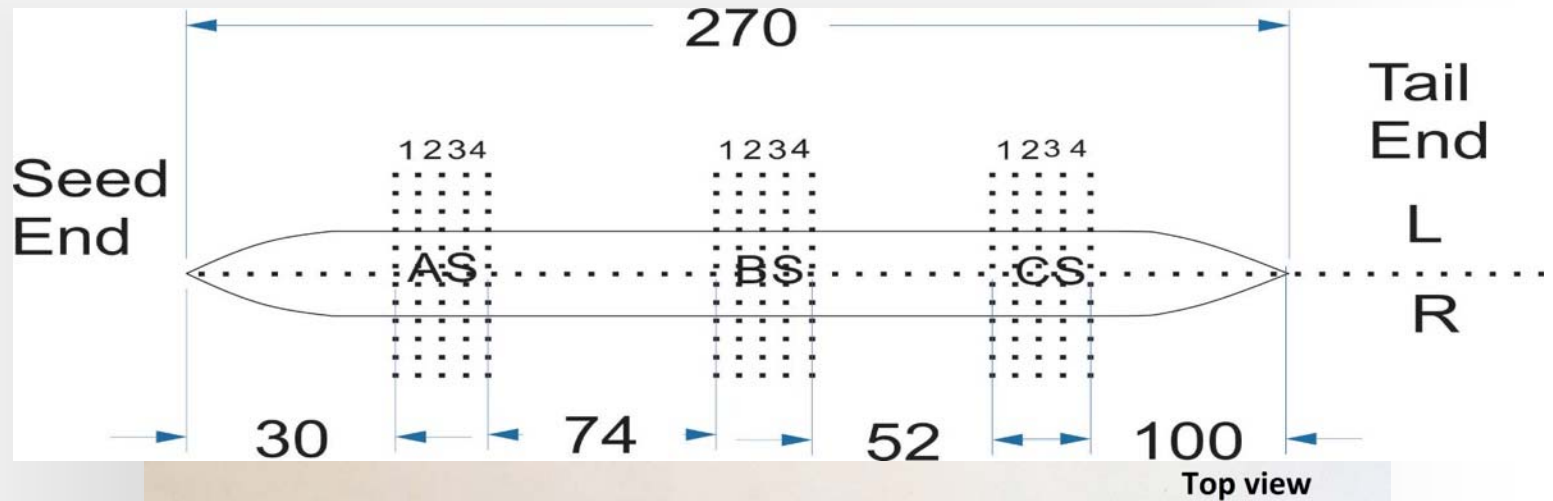
Oxygen: Instrumental Gas Analysis (IGA)

All others elements: GDMS

	Before		After
	Sample 1	Sample 2	
<i>O<sub>2</sub></i>	16 ppm	180 ppm	< 10 ppm
<i>Li</i>	< 10 ppb	< 10 ppb	< 10 ppb
<i>B</i>	< 10 ppb	11 ppb	< 10 ppb
<i>Na</i>	30 ppb	20 ppb	< 10 ppb
<i>Mg</i>	30 ppb	20 ppb	< 10 ppb
<i>Al</i>	30 ppb	180 ppb	< 10 ppb
<i>Si</i>	230 ppb	620 ppb	530 ppb
<i>S</i>	220 ppb	240 ppb	20 ppb
<i>Cl</i>	50 ppb	130 ppb	20 ppb
<i>Ca</i>	60 ppb	50 ppb	20 ppb
<i>Ti</i>	120 ppb	10 ppb	< 10 ppb
<i>Cr</i>	10 ppb	< 10 ppb	< 10 ppb
<i>Fe</i>	40 ppb	80 ppb	< 10 ppb
<i>Ni</i>	< 10 ppb	10 ppb	< 10 ppb
<i>Cu</i>	20 ppb	10 ppb	< 10 ppb
<i>Zn</i>	50 ppb	80 ppb	< 10 ppb

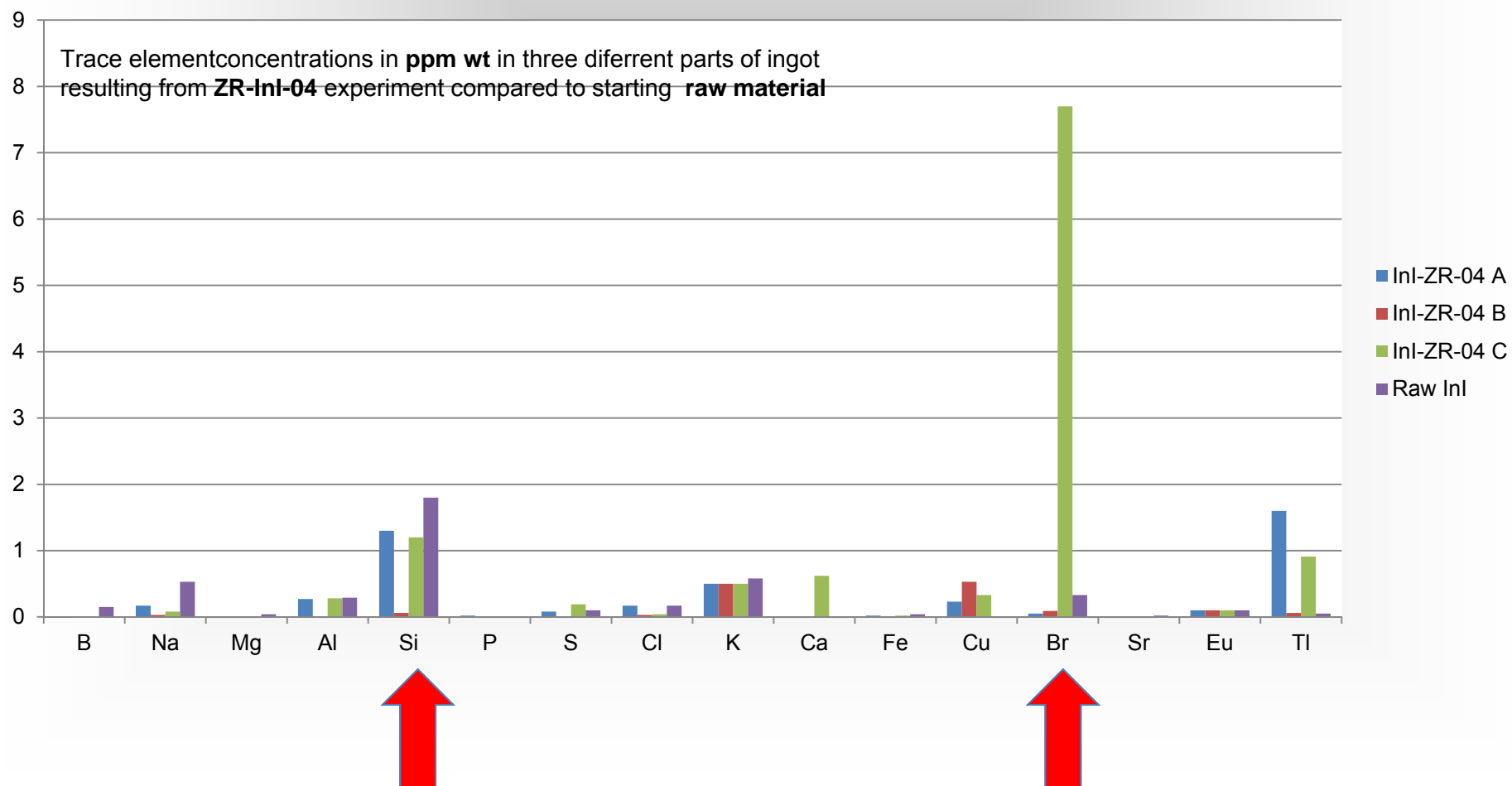
## RMD 2015

- Zone Refining (ZR)
- Bubbling  $\text{Ar}+5\% \text{H}_2$  through the melt



## RMD 2015: Zone Refining (ZR)

Charge: InI (Sigma Aldrich, 99.999 %)



Inl  
#4 InI-ZR-05 A

Sample ID:

20-Jul-15

Inl

Job #

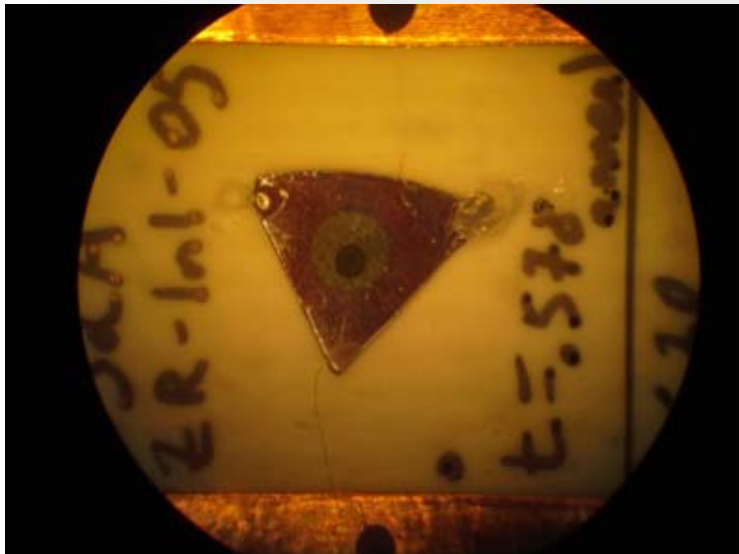
Sample ID:

#2 InI-ZR-04 B

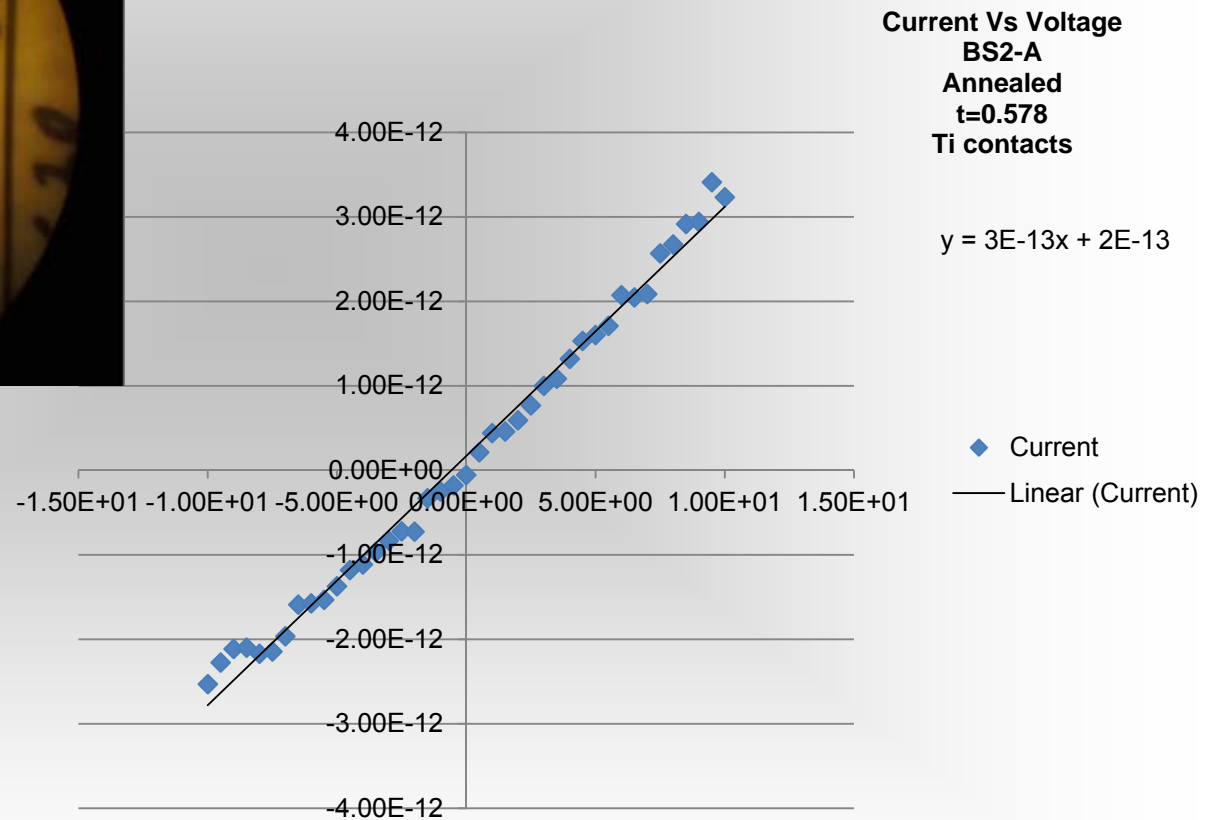
Element	Concentration [ ppm wt ]	Element	Concentration [ ppm wt ]
Li	< 0.01	Ag	< 0.05
Be	< 0.01	Cd	< 1
B	< 0.01	In	Matrix
F	< 0.5	Sn	< 0.5
Na	0.02	Sb	< 0.1
Mg	0.04	Te	< 0.5
Al	1.1	I	Matrix
Si	1.8	Cs	< 1
P	< 0.01	Ba	< 0.1
S	0.24	La	< 0.05
Cl	0.02	Ce	< 0.05
K	< 0.5	Pr	< 0.05
Ca	< 0.01	Nd	< 0.01
Sc	< 0.01	Sm	< 0.01
Ti	< 0.01	Eu	0.16
V	< 0.01	Gd	< 0.01
Cr	< 0.01	Tb	< 0.01
Mn	< 0.01	Dy	< 0.01
Fe	0.03	Ho	< 0.01
Co	< 0.01	Er	< 0.01
Ni	< 0.01	Tm	< 0.01
Cu	< 0.01	Yb	< 0.01
Zn	< 0.01	Lu	< 0.05
Ga	< 0.05	Hf	< 0.01
Ge	< 0.05	Ta	Source
As	< 0.05	W	< 0.01
Se	< 0.1	Re	< 0.01
Br	1.3	Os	< 0.01
Rb	< 0.01	Ir	< 0.05
Sr	< 0.01	Pt	< 0.1
Y	< 0.01	Au	< 0.1
Zr	< 0.01	Hg	< 0.05
Nb	< 0.01	Tl	0.91
Mo	< 0.01	Pb	< 0.05
Ru	< 0.01	Bi	< 0.05
Rh	< 0.01	Th	< 0.01
Pd	< 0.05	U	< 0.01

Element	Concentration [ ppm wt ]	Element	Concentration [ ppm wt ]
Li	< 0.01	Ag	< 0.05
Be	< 0.01	Cd	< 1
B	< 0.01	In	Matrix
F	< 0.5	Sn	< 0.5
Na	0.03	Sb	< 0.1
Mg	< 0.01	Te	< 0.5
Al	< 0.01	I	Matrix
Si	0.06	Cs	< 1
P	< 0.01	Ba	< 0.1
S	< 0.01	La	< 0.05
Cl	0.03	Ce	< 0.05
K	< 0.5	Pr	< 0.05
Ca	< 0.01	Nd	< 0.01
Sc	< 0.01	Sm	< 0.01
Ti	< 0.01	Eu	< 0.1
V	< 0.01	Gd	< 0.01
Cr	< 0.01	Tb	< 0.01
Mn	< 0.01	Dy	< 0.01
Fe	< 0.01	Ho	< 0.01
Co	< 0.01	Er	< 0.01
Ni	< 0.01	Tm	< 0.01
Cu	0.53	Yb	< 0.01
Zn	< 0.01	Lu	< 0.05
Ga	< 0.05	Hf	< 0.01
Ge	< 0.05	Ta	Source
As	< 0.05	W	< 0.01
Se	< 0.1	Re	< 0.01
Br	0.09	Os	< 0.01
Rb	< 0.01	Ir	< 0.05
Sr	< 0.01	Pt	< 0.1
Y	< 0.01	Au	< 0.1
Zr	< 0.01	Hg	< 0.05
Nb	< 0.01	Tl	0.06
Mo	< 0.01	Pb	< 0.05
Ru	< 0.01	Bi	< 0.05
Rh	< 0.01	Th	< 0.01
Pd	< 0.05	U	< 0.01

# I-V curve of detector *BS2-A\_(annealed)*:



$$d_{\text{contact}} = 3\text{mm}$$



$$\rho_{\text{BS2-A}} = 4.07 \times 10^{12} \Omega \text{ cm}$$

Material	Cd <sub>0.9</sub> Zn <sub>0.1</sub> Te (CZT)	Hgl <sub>2</sub>	InI
Average atomic number, Z	49.1	62	51
Density, g/cm <sup>3</sup>	5.78	6.4	5.31
Band gap, eV	1.55	2.14	2.0
Melting point, °C	~1100	259	351
Structure	Zincblende	Tetrahedral- layered	Orthorhombic
Knoop Hardness, kg/mm <sup>2</sup>	92	10	27
Molecule Disassoc. Energy eV	1.2	0.35	3.43
Herzberg's tables [19]			
Electrical Resistivity, Ohm-cm	3 x10 <sup>10</sup>	10 <sup>13</sup> to 10 <sup>14</sup>	1x10 <sup>11</sup>



$$\rho \approx 4 \times 10^{12}$$

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CASIS/NASA, 2015: “Detached Melt and Vapor Growth of InI in SUBSA Hardware”

**(a) Detached directional solidification: 3 crystals**

*Improve crystalline perfection*

*Observe the dewetting process in microgravity*

**(b) Physical vapor transport growth: 3 crystals.**